National Bureau of Standards

TECHNICAL NEWS BULLETIN

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Thermal Decomposition of High Polymers

A new method for investigating the composition and properties of high polymers has been developed by S. L. Madorsky and Sidney Straus of the National Bureau of Standards in connection with a program for the study of the structure of natural and synthetic rubbers. The procedure consists in the pyrolysis, or thermal decomposition, of the polymer under high vacuum with subsequent separation of the products into gaseous, liquid, and semisolid fractions for analysis.

Polymeric substances—such as polystyrene, neoprene, rubber, nylon, lucite, and many others—owe their unusual strength, elasticity, and plasticity to the long, chainlike structure of their molecules. Such compounds are formed in nature or in the laboratory by a process known as polymerization, in which sometimes as many as several million individual molecules (monomers) are joined by chemical reaction. Many polymers are made up of two different types of monomers and are known as copolymers. An example is GR–S synthetic rubber, which is formed by polymerization of a mixture of styrene and butadiene.

One of the most effective means for obtaining information on the structure of polymers and copolymers is thermal decomposition of a sample under conditions of molecular distillation in the absence of oxygen or other reactive substances. The term molecular distillation has been applied to that type of distillation where there is no return of escaping molecules to the evaporating surface. This is ordinarily accomplished by operating with high-boiling (low-vapor pressure) liquids under such high vacuum that the mean free path of the escaping molecules is of the order of the distance between the surface of the evaporating liquid and the cooled condensing surface of the still. Under these conditions in pyrolysis, the fragments into which the polymeric chain is decomposed by heat may be distilled and collected without further fragmentation due to molecular collision. From a study of the way in which the polymeric chain breaks up—as shown by the length and type of fragments formed, the relative amounts of monomeric to longer fragments, and similar data—much can be learned about the arrangement of the monomeric units in the chain and the relative strength of the chemical bonds involved. Pyrolysis also provides a means for determining optimum conditions for recovery of the component monomers from scrap polymeric substances.

The apparatus developed at the Bureau consists essentially of a double-walled cylindrical flask similar to a Dewar flask, except that the inner vessel is joined to the outer jacket by a ground-glass joint. The space between the cylinders is evacuated to a pressure of one millionth of a millimeter of mercury and is connected, by means of a side arm, to receivers for the various fractions. At the bottom of this space is a small tray on which a thin layer (25 to 50 milligrams) of the polymer is heated to between 300° and 400° C by means of platinum-wire helices encased in short lengths of glass tubing. During pyrolysis the outer wall of the flask is cooled by water flowing through spiral tubing surrounding the vessel.

Liquid air is first placed in the inner cylinder, and the temperature of the sample is then raised to the point

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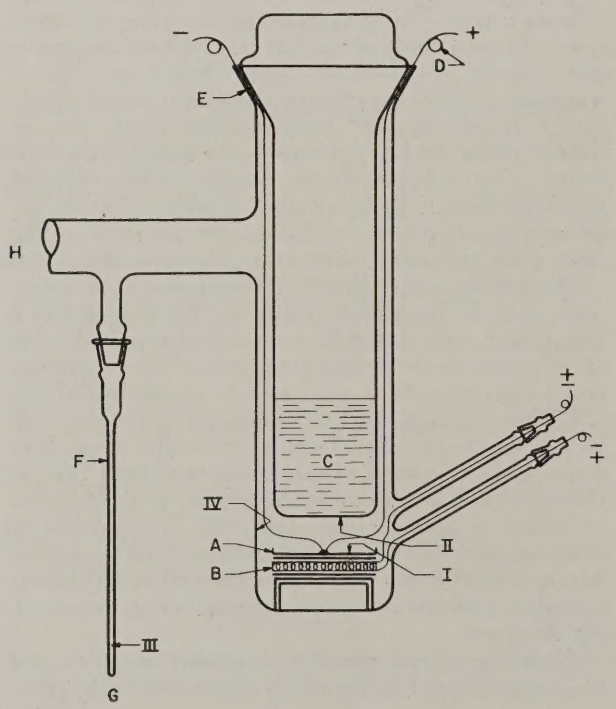
of decomposition. All the products of pyrolysis, except those which do not condense at liquid-air temperature, then collect on the inner wall while the more volatile material is allowed to expand into a receiver. This gaseous fraction is analyzed in the mass spectrometer; its weight can then be calculated from volume, pressure, and composition.

To separate other fractions, the liquid air is removed from the central cylinder, and the temperature of this cylinder is raised in steps by the substitution of other refrigerants, such as dry ice, until room temperature is reached. This permits fractions that are volatile at temperatures between liquid-air and room temperature to distill over into liquid-fraction receivers, each of which is maintained at the temperature of liquid air. The condensate on the inner wall, volatile at the temperature of pyrolysis but not at room temperature, is obtained as one fraction by dissolving it with benzene, collecting in a platinum crucible, and vaporizing the benzene.

Additional fractions are provided by the semisolid residue in the tray and the deposit, nonvolatile at room temperature, which condenses on the outer wall of the evacuated space. This latter fraction, which may safely be assumed to have the same composition as the deposit on the liquid-air chamber, is not collected, but its weight is calculated by subtraction of the weights of the other fractions from that of the sample. The gaseous and liquid fractions thus obtained are analyzed in the mass spectrometer, and the semisolid fractions are identified by other physical and chemical methods of analysis.

Because of its relatively simple structure, polystyrene was the first polymer selected for study. This compound was found to break up at the temperature of pyrolysis into the monomer, dimer, trimer, and some tetramer. The most striking observation was the consistency with which only small fragments, none longer than the tetramer, were obtained. Doubtless the larger molecular fragments became entangled in the mass of long-chain polystyrene molecules and were held until they decomposed further into shorter lengths.

The program now under way at the Bureau includes fragmentation studies of polybutadiene, polyisoprene, natural and synthetic rubbers, nylon, and "popcorn" polystyrene. Efforts will be made to develop techniques that will provide longer-chain fragments for analysis. Plans are also in progress for carrying out similar experiments on a much larger scale with samples of several hundred grams. This will permit the collection of fractions of a size more convenient for chemical analysis and physical tests.



In the Bureau's study of high-polymer structure, a thin layer is heated to decomposition under high vacuum on tray *A*. Fraction II condenses on liquid-air chamber *C*; a more volatile fraction expands through *H* into a receiver. Removal of liquid air permits collection of fraction III (volatile at room temperature) in *G*. The tray residue and the outer-wall condensate constitute fractions I and IV. Gaseous and liquid fractions are analyzed in the mass spectrometer, semisolid fractions by other means.

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X-Ray Diffraction Standards

An indexed compilation of X-ray diffraction measurements for almost 3,000 different powdered chemical compounds has been made available, in card form, through a cooperative program sponsored by the American Society for Testing Materials and the American Society for X-Ray and Electron Diffraction. Since the interplanar spacings and intensities presented for each of these 3,000 materials are strictly characteristic of that compound, identification is as positive as fingerprinting. The National Bureau of Standards is directing a project, under H. E. Swanson, to increase materially the number of indexed substances and to improve the accuracy of existing data.

The regular arrangement of component atoms is a characteristic property of a crystalline material. Since the wavelength of X-rays is of the same order of magnitude as the interatomic spacing in crystals, these rays, when directed through such substances, are diffracted by the crystals, which act as a three-dimensional diffraction grating. For any particular crystalline species, the angles and intensities of the diffracted beam provide a unique pattern, and hence a useful and positive means of identification.

This method of identification of crystalline substances (and almost all solids except glasses are crystalline in some degree) has certain definite advantages over ordinary chemical analysis. As the results are obtained directly in terms of compounds rather than elements or oxides, X-ray diffraction patterns indicate the particular crystal form or hydrate of a compound and, in the case of mixtures, give the form of both compounds.

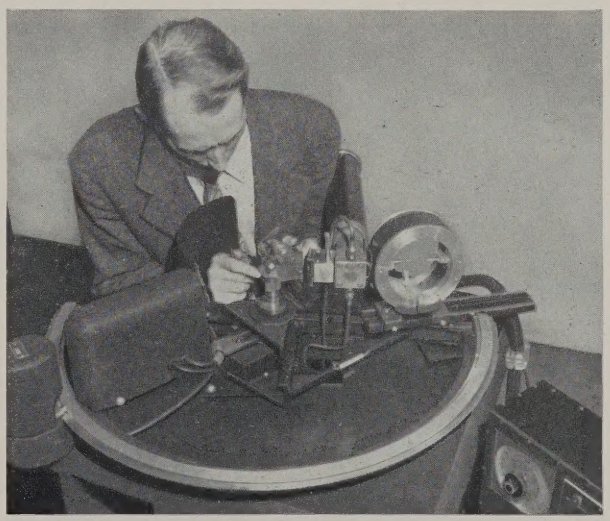
The usefulness of X-rays in the laboratory for chemical analyses increases in proportion to the growth and effectiveness of the expanding index upon which it is more or less dependent. Accurate X-ray diffraction data—recorded in terms of interplanar spacings in angstrom units, and relative intensities of the diffraction lines—must, therefore, be available on the widest possible number of substances. Compounds to be useful as diffraction standards must be identified with certainty as well as free from impurities. It has been shown that a small percentage of the X-ray diffraction index contains data that are conflicting or misleading. This has come about as a natural development over a period of years, in the process of gathering all published material. Where specific data have been questioned, the Bureau's diffraction laboratory is attempting to present the correct information.

Improvements in equipment and techniques being made at the National Bureau of Standards and elsewhere are contributing to increased accuracy of X-ray diffraction data. The use of the Geiger counter for detecting X-ray diffraction effects has made closer measurement of atomic spacing possible. Commercial Geiger counter equipment modified by the Bureau's microscopic and diffraction analysis laboratory permits the measurement of a considerably extended range of diffraction angles. This is particularly useful in determining small changes in unit cell size which sometimes occur in solid solution series. Although the Geiger counter technique is definitely better than the photographic methods commonly used, certain precautions must be observed because of the use of flat specimens with the Geiger counter and of focusing conditions. Spacing corrections are sometimes necessary to allow for X-ray beam absorption in specimens of low atomic weight. The possibility of preferred orientation of the specimens is greater, and special care must be taken to avoid the errors in relative intensity resulting from this effect.

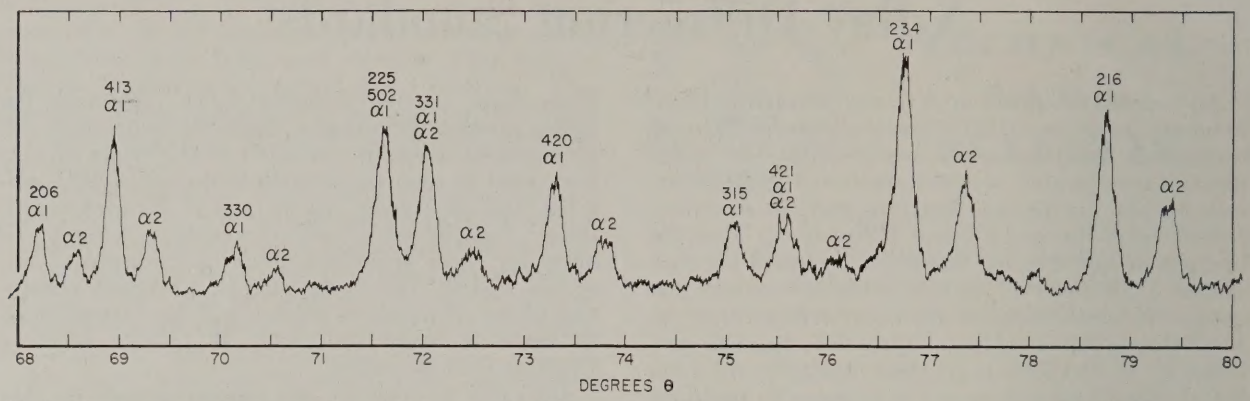
The NBS microscopic and diffraction analysis laboratory has adopted a practice of analyzing, for record, specimens prepared under almost opposite conditions—one showing as complete randomness of orientation as possible and the other smoothly packed to present an effective flat surface. This procedure is not necessary for routine analyses, but is useful, since the data will be used under varying conditions. In preparing diffraction data for general use, it is important that such practices be followed, so that the resulting measurements will be interchangeable regardless of the type of equipment employed. This is usually accomplished by working toward data that are not influenced by inherent differences in equipment.

Crystalline substances, particularly minerals, are often identified by measurement of their indices of refraction and other optical properties. When applicable, optical properties are measured on the same samples used in the X-ray study, thus providing additional determinative data and a check on the proper identity of the sample.

Since the care necessary in choosing high-purity compounds is not as great as for spectrographic analysis, samples are chosen first for absolute identity and sec-



Modified Geiger-counter equipment is used at the Bureau for cataloging X-ray diffraction data. Modifications include an arc of 180° in place of the usual 90° arc, a more powerful X-ray tube, and motion of the specimen (small white square near center) during measurement.

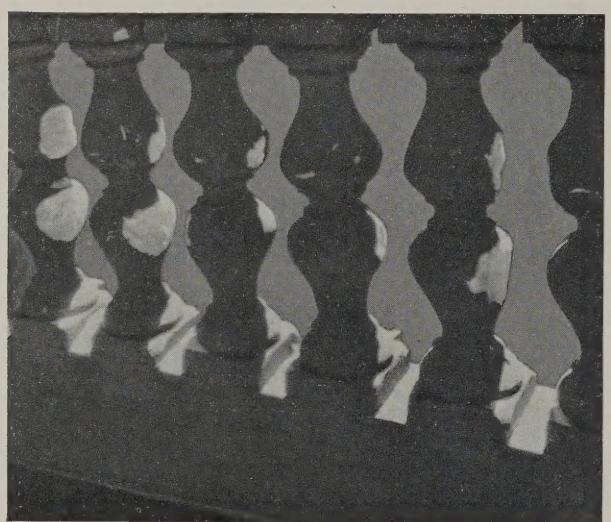


As the Geiger counter moves through the arc, the X-ray diffraction pattern is automatically recorded. The peaks show the angle of the diffracted beam by their position and the intensity by their height. Identification of chemical compounds by X-ray diffraction data is as positive as fingerprinting. A portion of the back-reflection part of the pattern of quartz (reduced scale drawing) shows plainly the resolution of the $K\alpha_1$ and $K\alpha_2$ doublet.

ondly for freedom from impurities. In practically all cases the sources of samples for this work are the various cooperating industrial laboratories that have special interests in carefully synthesizing certain chemicals. In fact, the first substantial contribution of diffraction data on about 1,000 substances was made in 1938 by the Dow Chemical Co. As a further check on the identity of a compound, samples are considered from different sources. Laboratories preparing chemicals that may serve as a basis for diffraction data are invited to contribute small samples to the National Bureau of Standards for this purpose.

Growth of Marble as a Basis for Durability Tests

The deterioration of some of our important marble structures shows that there is a need for better methods of selecting marble for durability. Laboratory studies on the basic causes of marble weathering, under the direction of D. W. Kessler of the Bureau's building stone laboratory, indicate that the principal destructive force results from temperature cycles that produce a permanent growth of the marble, that is, an actual increase in volume. Growth of marble is accompanied by decreases in structural properties such as strength, coherence, and elasticity—effects that are confirmed by examination of marble from old structures. Not all marbles, however, exhibit the same rate of growth or the same rate of deterioration. Although the phenomenon has been known for many years, it is only recently that this property has been investigated as the basis of a durability test for selection of marbles.



Extensive damage to marble structures often results from "sugaring" or crumbling of the marble. Good correlation has been obtained between results of a laboratory test developed at the Bureau for predicting this behavior and observations on weathered structures.

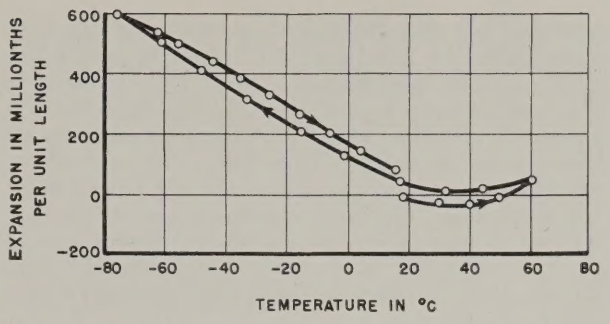
Acid rain water has long been considered the principal destructive agent on marble. Laboratory tests based on this theory, however, have not proved satisfactory for distinguishing between the good and poor grades. Acid rain water produces a surface effect that will destroy a polish within a short time, but old weathered marbles usually show a granulated effect, commonly called "sugaring," that is much more serious. Sugaring is not confined to the surface but affects the interior of marble blocks almost as rapidly as the surface. Finally a sand, in which most of the grains show no acid action, is produced. Some of the less durable marbles have reached this condition in less than 50 years.

Most marbles are composed mainly of calcite, with several other minerals usually present in small amounts. The calcite crystals are so closely interlaced that the porosity of most varieties is less than 1 percent. Although the mineral impurities are commonly of a weather-resistant nature, some are less stable than calcite.

The underlying cause of sugaring seems to be the peculiar thermal expansion of calcite crystals. When

heated, each crystal expands along one axis and contracts along another. On cooling, the opposite effects occur. In a mass of tightly interlaced calcite crystals, each temperature change produces complex stresses and slippage between the crystals. The permanent increase in volume is believed to represent the amount by which the crystals fail to regain their original positions after they have been moved out of place by a temperature change. Increases in volume of as much as 60 cubic inches in a cubic foot (3½%) have been noted in some weathered samples. Eventually, the bond between the crystals may be completely broken, and crumbling results.

The effects of heating cycles readily become apparent in the laboratory, and the changes in volume can be measured. These effects are being studied at the Bureau on a series of marbles to determine if the rates of change for heating cycles can be correlated with observations on the same materials under exposure to the weather. On the basis of observations made so far on weathered structures, the correlations have been satisfactory. Additional data showing effects of actual weathering are being accumulated.



The principal destructive force in marble weathering appears to result from temperature cycles that produce a permanent growth of the marble. This effect is readily demonstrated by the expansion curve of a typical marble on heating and cooling.

Double Freezing Point Method for Styrene Purity

A simple method for the determination of the purity of styrene, particularly adapted to industrial process control, has been developed by Dr. J. F. Masi of the National Bureau of Standards. The method utilizes an empirical equation relating the percentage of styrene by weight in the sample to two freezing points obtained experimentally with specially designed apparatus. One of these freezing points is taken on a part of the original sample, and the other is determined from a portion of the sample from which the more volatile hydrocarbon impurities have been removed by evaporating and recondensing the styrene. This procedure, which was devised for the Office of Rubber Reserve, is now in use in all of the Government-controlled plants making GR–S synthetic rubber.

GR–S rubber is produced by the polymerization of a mixture of styrene and butadiene. The styrene that is fed to the reactors in the manufacturing process is a blend of fresh styrene with that recovered by steam distillation at the end of the reaction. Fresh styrene is pure, except for a residue of less than 1 percent of the ethylbenzene from which it is obtained, but recovered (or "recycle") styrene contains no more than 85 to 90 percent of the pure substance. For calculation of plant inventories and plant efficiencies, and in order to produce rubber of uniformly high quality, it is necessary to know the purities of both the fresh and recycle styrene and to closely control the amount of styrene in the blend made from them.

Measurement of freezing point depressions is one of the most convenient ways of determining the purity of hydrocarbon compounds. However, for routine work in industrial laboratories the necessary time, personnel, and equipment are not always available for the more accurate technique using platinum resistance thermometers. The National Bureau of Standards has therefore developed a practical freezing point procedure that may be applied effectively by an operator who lacks technical training.

The principal impurities in recycle styrene are ethylbenzene, 4-vinyl-cyclohexene (butadiene dimer), and 1,3-butadiene; comparatively small amounts of other hydrocarbons are also present. A single good freezing-point value would suffice to determine the purity of a styrene sample if only the molecular percentage purity were desired and if all of the impurities formed ideal solutions with styrene. However, in practice it is necessary to know the percentage purity by weight; moreover, ethylbenzene and 1,3-butadiene do not form ideal solutions with styrene. The difficulties are overcome in the method developed at the Bureau by removing the butadiene and any other volatile impurities and obtaining the freezing point of the mixture of styrene, ethylbenzene, and 4-vinylcylohexene which remains. This freezing point, together with the freezing point of the original sample, is then used to calculate the purity of the styrene.

The separation of low boiling impurities is accomplished by completely evaporating a 15-ml portion of the sample under low pressure and passing the vapor through a trap kept at −65° C. The styrene, ethylbenzene, and 4-vinylcyclohexene solidify on the walls of the trap, and the light hydrocarbons pass through without condensing. The apparatus required is easily constructed and produces more efficient separation than ordinary distillation. The empirical equation relating the weight percentage of styrene to the two freezing points assumes that no important impurities other than those mentioned are present and that ethylbenzene and 4-vinylcyclohexene occur in nearly equal amounts. The application of this equation is greatly simplified by the use of a large-scale nomogram prepared for the convenience of industrial laboratories.

The freezing points are obtained by a procedure de-

signed to provide the highest possible accuracy consistent with the rapid taking of observations by relatively untrained personnel. The styrene is placed in the innermost of a nest of three test tubes immersed in a chloroform-carbon tetrachloride freezing mixture contained in an unsilvered Dewar flask. Throughout the determination, the sample is stirred at the rate of about 150 strokes per minute by a motor-driven stirrer, and the bath is maintained (by addition of small pieces of dry ice) within 0.5° C of a temperature selected so that the rate of cooling of the sample, while freezing, is near 0.1° C per minute.

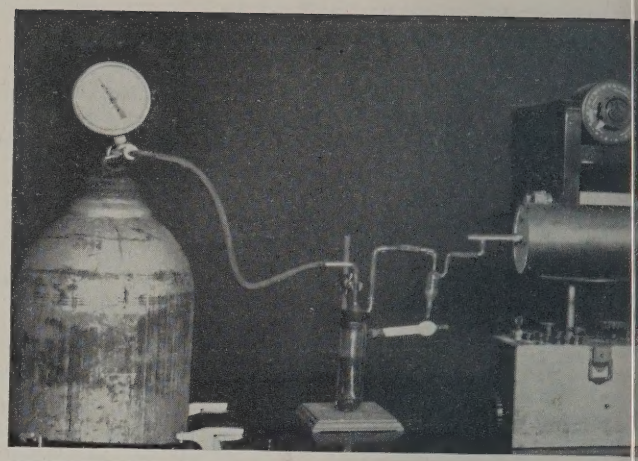
The temperature of the sample is observed every half-minute as it is being cooled, beginning a few minutes before freezing is expected to occur and continuing at least 10 minutes after freezing begins. As some undercooling always takes place, the actual freezing point is found by extrapolating the freezing curve back to the liquid cooling curve. This extrapolation is best performed by a geometrical construction proposed by Taylor and Rossini.[1] The freezing point obtained by extrapolation is then corrected by applying the thermometer-calibration and emergent-stem corrections.

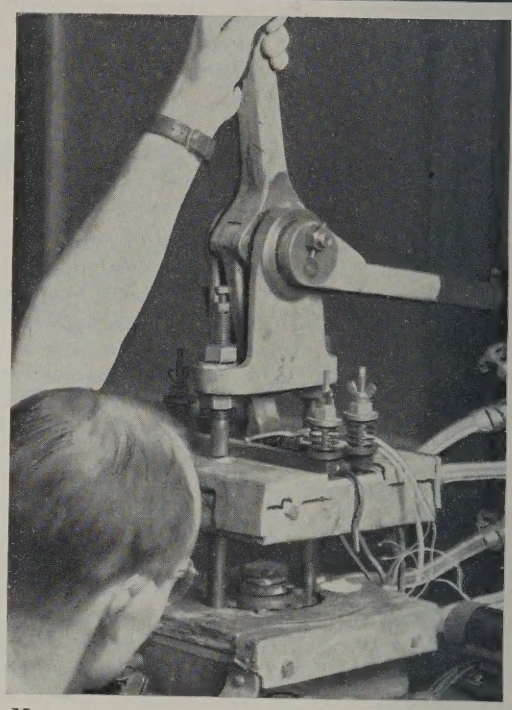
In order to realize the greatest possible accuracy in this work, a liquid-in-glass thermometer readable to 0.01°C has been designed at the National Bureau of Standards. The thermometric liquid is a thallium amalgam that remains fluid below the lowest temperatures likely to be encountered in styrene analyses. Thermometers of this type are now available commercially and may be calibrated by the Bureau.

The accuracy of the freezing points is also enhanced by frequently checking the apparatus and procedure with a material of known freezing point. Bromobenzene is excellent for this purpose as it is available in purity greater than 99 percent and does not readily deteriorate. The freezing point of bromobenzene is −30.75° C, and that of pure styrene is −30.63° C.

Sixty-eight styrene solutions containing various amounts of ethylbenzene, 4-vinylcyclohexene, and 1,3-butadiene were employed in investigating the method and in developing the empirical equation for calculating styrene purity from the two freezing points. The reproducibility of freezing points of the same solution, when obtained by different operators using different thermometers, is within 0.03° C. The efficiency of separation of butadiene was judged by comparison of freezing points obtained before adding, and after removing, butadiene. These experiments indicate that variation in the amount of butadiene (up to 3%) does not affect the sharpness of separation, but it was found that a large concentration of the heavier impurities may cause a small amount of the 4-vinylcyclohexene to be pumped out during the separation and thus to be calculated as butadiene. From a consideration of the assumptions involved and the deviation of calculated from actual percentages of styrene in the prepared solutions, the probable error of the method is estimated at ±0.15 percent of styrene for 90-percent styrene solutions.

[1] W. J. Taylor and F. D. Rossini, J. Research NBS **32**, 197 (1944) RP1585.

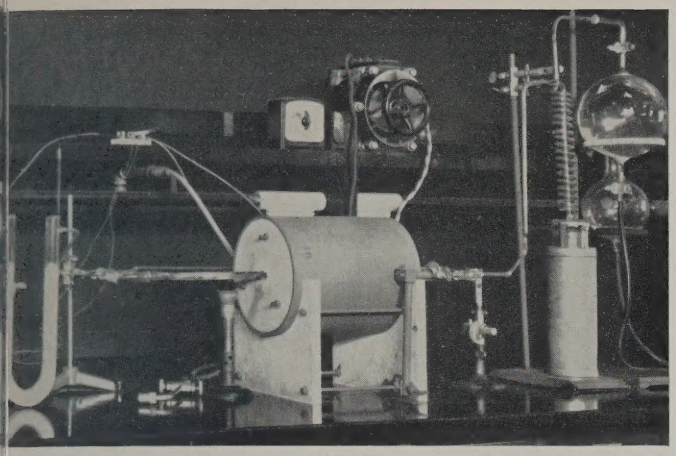


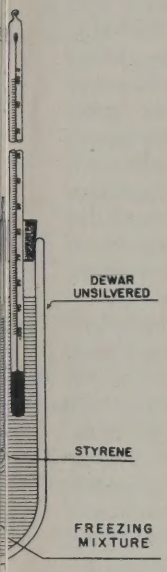


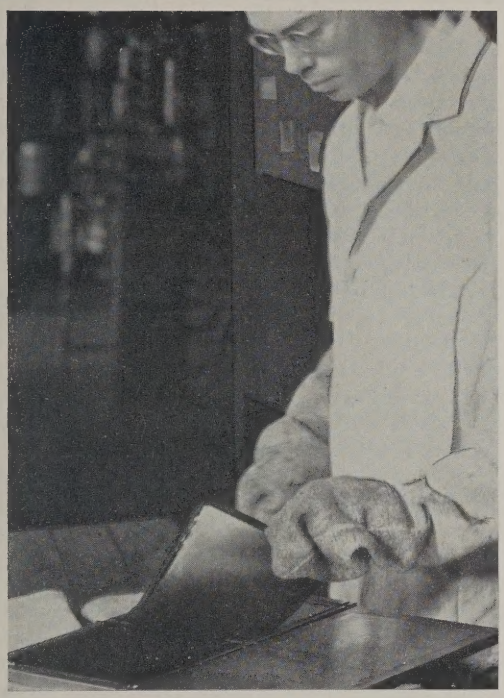
Measurement of the purity of styrene by means of freezi in organic compounds (top) are among the analytical pr of research on synthetic rubber. Other phases of this p (lower left), and the effects of compounding (vulcanized

Direct Determinatic Con

An improved technique for the direct determination of oxygen in high-molecular weight organic compounds has been developed by W. W. Walton, F. W. McCulloch, and W. H. Smith of the National Bureau of Standards. By this method, small amounts of oxygen, such as occur in natural and synthetic rubbers, in plastics prepared from hydrocarbons, and in mineral oils, can be measured with precision and accuracy. Essential features of the procedure are thermal decomposition of the







it data (lower center) and the direct determination of oxygen developed by the National Bureau of Standards in its program include the study of properties of the rubber, such as viscosity on, lower right).

# of Oxygen in Organic unds

sample in an atmosphere of oxygen-free helium and conversion of the resulting oxygen compounds to carbon monoxide by passage of the products over carbon at 1,120° C. The oxygen content of the material is then calculated from the percentage by volume of carbon monoxide in the collected gas as determined by the NBS carbon monoxide indicator.

In the analysis of organic compounds, the amounts of elements other than oxygen have always been determined directly, and that of oxygen has been determined by difference. The value for oxygen obtained in this way, involving an accumulation of possible errors in the determinations of the other elements, has proved reasonably satisfactory in investigations of the structure of compounds of low molecular weight. However, for the analysis of compounds of high molecular weight or of substances containing very small amounts of oxygen, greater accuracy becomes necessary. In recent years, the need for a direct oxygen method has been especially pronounced in the fields of high-polymer plastics and synthetic rubber. Oxygen determination is important, for example, in studying the effects of various agents added to retard aging of rubber and in ascertaining the influence of small amounts of oxygen on the physical properties of this substance relative to processing and vulcanization, as well as in the basic study of the composition of the polymer. Likewise, in the analysis of synthetic rubber there is need for extremely close agreement among values obtained by various laboratories in order that rubber produced by different plants may be interchangeable. The procedure developed at the Bureau is a modification of the micro method developed by Unterzaucher.[2] It is expected to aid materially in this work, and it is believed that the method may be readily adapted to analysis of compounds containing large amounts of oxygen.

The apparatus consists primarily of a helium tank with pressure regulator, a furnace at 400° C packed with copper spirals through which the helium is passed to remove oxygen, a U-tube filled with ascarite, and a drying agent to absorb carbon dioxide and moisture from the helium, a quartz tube having a section packed with carbon pellets, a tubular furnace enclosing that section of the quartz tube and heated to 1,120° C, and a flask of accurately measured volume in which the carbon monoxide is collected.

The apparatus is arranged so that a continuous stream of helium is passed over the heated copper and through the drying agents into the quartz tube. After the weighed sample has been placed in the entrance end of the tube on a platinum boat, air is swept out of the system by means of a reverse stream of heated helium for 2 hours. The flow of helium is then directed forward through the high-temperature furnace toward the collecting flask.

The sample is burned by slowly advancing a Bunsen burner and a gauze mantle along the section of the quartz tube containing the platinum boat. This operation, requiring about 10 minutes, is repeated to insure complete decomposition of any particles that may have sublimed to other parts of the tube.

The products of pyrolysis pass with the helium over the hot carbon in the furnace and through a liquid air trap to the collection flask, where water is gradually displaced by the mixture of gases. After a given volume of gas has been collected, as measured by the water level in a capillary, the collecting flask is disconnected and a stopcock opened momentarily, allowing a small amount of air to flow into the flask to restore

[2] J. Unterzaucher, Ber. deut. chem. Ges. **73B**, 391 (1940).

atmospheric pressure. To determine the percentage by volume of carbon monoxide in the collected gas, the flask is connected through a flow meter to an NBS carbon monoxide indicating tube, which contains a colorimetric indicating gel capable of detecting and estimating less than 1 part of carbon monoxide in 500 million parts of air. After the gas has passed through the tube at the rate of 70 ml per minute for a definite period, the color shown by the indicating tube is compared visually with standard tubes prepared at the same time by passing known amounts of carbon monoxide through them. From the value obtained for the volume concentration of carbon monoxide in the collected gas, the volume of the gas (which is known by previous calibration of the flask), the density of carbon monoxide, and the weight of the sample, it is possible to calculate the percentage of oxygen in the material.

This method has been used with excellent results at the Bureau in the analysis of compounds containing less than 2 percent of oxygen, and it is expected that with some modification the procedure may be used in the analysis of materials containing higher percentages of the element. Since accurate determination of carbon monoxide in large quantities is not practicable, the carbon monoxide might first be oxidized to carbon dioxide, which could then be measured by standard methods.

Boron-Treated Steels

It is now recognized that the hardenability of some types of steel is materially improved by the addition of small amounts of boron. Apparently the effectiveness of the treatment with boron depends upon the steelmaking practice, and the amount and form of boron retained in the steels. The optimum effect on hardenability is obtained when boron is added in the form of simple or complex ferroalloys, commonly called "intensifiers," "special addition agents," or "needling agents," to thoroughly deoxidized heats in which the amount of boron recovered is within the range of about 0.001 to 0.005 percent. Because one of the main roles of alloying elements in steels is to increase the depth of hardening or hardenability, this significant effect of boron suggested the possibility that it might be substituted for a part or all of the strategic elements commonly used as alloying agents in steels. During the war, to offset possible shortages of these critical elements, an extensive investigation was undertaken at the National Bureau of Standards to determine quantitatively the effects of boron on some properties of steels used for armor plate and other military applications.

The program was divided into two main parts; namely, (1) a study of the interrelationship between boron, carbon, and alloying constituents on some of the properties of steels made in the laboratory, and (2) a study of the properties of boron-treated steels of selected chemical composition made commercially under predetermined deoxidizing practices. Special attention was also directed toward the development of spectrographic and chemical methods for the accurate determination of small amounts of boron in steel. The investigation [3] [4] was carried out at the National Bureau of Standards under the auspices of the War Metallurgy Committee, National Research Council, to which funds were transferred by the Office of Scientific Research and Development.

The work included a study of the cleanliness and structures of the steels as hot-rolled, normalized, and heat-treated. Determinations were made of the austenite and McQuaid-Ehn grain sizes, hardenability (Jominy), notch toughness (Charpy impact) at room and low temperatures, and tensile properties at room temperature. The investigation was extended with experimental steels to include a study of the effect of deoxidation practice and composition of ferroalloys containing boron, on the recovery of boron and its influence on the above properties; a determination of the recovery of boron on remelting in an induction furnace under both slightly and strongly deoxidizing conditions; and the determination of the effect of boron on the transformation temperatures and weldability of some of the experimental steels.

Approximately 250 experimental steels were made as "split" heats in an induction furnace and 20 commercial steels as a split heat in a basic open hearth furnace. Thus, a steel from each heat was prepared without boron (except in a few special cases) and used as a basis for determining the magnitude of the effect of boron on the mechanical properties.

Boron was determined chemically by a distillation-colorimetric method, using phosphoric acid and turmeric, with an accuracy of ± 0.0002 percent of boron in the lower part of the range from 0.0005 to 0.006 percent, and an accuracy of ± 0.0005 percent in the upper part of this range. The average difference between determinations by chemical and spectrographic methods was about 0.0003 percent of boron.

Initially normalized specimens, quenched from the usually recommended temperature range, were subjected to end-quench tests for hardenability (Jominy method). Although the relative hardenability of the various steels is obtained by a comparison of the Jominy curves, it is considerably more convenient to show the magnitude of the hardenability effect due to boron (or other variable) from heat to heat by comparing the distances from the quenched end of the Jominy bars corresponding to the same selected hardness values or structures. Comparisons, therefore, are made of the hardenability of the various steels on the basis of the distances from the quenched end of the bar for hardness

[3] For further technical details see, Influence of boron on some properties of experimental and commercial steel by Thomas G. Digges and Fred M. Reinhart, J. Research NBS **39**, 67 (1947) RP1815. Reprints may be obtained from the Superintendent of Documents, Government Printing Office, Washington 25, D. C., at 30 cents each.

[4] The plans for the investigation were prepared jointly with a representative of the War Metallurgy Committee. The testing program for the commercial steels was prepared with, and approved by, the Subcommittee on Special Addition Agent Steels of the War Engineering Board, Iron and Steel Committee, and Army Ordnance.

values corresponding to both 50 and 95 percent of martensite.

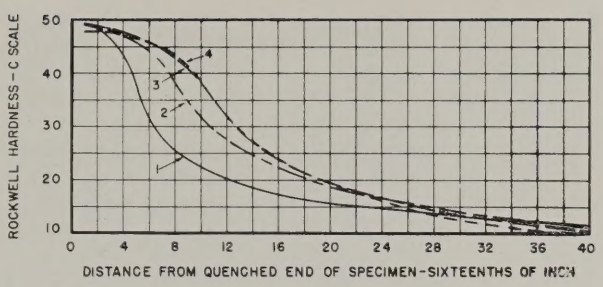
Charpy impact tests for notch toughness were made with quenched and tempered specimens. Tests were carried out in duplicate at room and low temperatures in a Charpy machine of 224.1 ft/lb capacity, with a striking velocity of the hammer of 16.85 ft/sec. The procedure for making the tests at low temperature consisted of cooling the specimens in an insulated bath containing equal parts of carbon tetrachloride and chloroform for a minimum of 30 minutes at the desired temperature, and then quickly transferring to the impact machine and breaking. The desired temperatures were obtained by regulated additions of solid carbon dioxide, and as this material passes directly from the solid to a gas, no dilution occurred in the liquid bath. The temperature of the cooling bath was measured by means of a copper-constantan thermocouple and an indicating potentiometer. Rockwell "C" hardness was measured on the fractured specimens at room temperature.

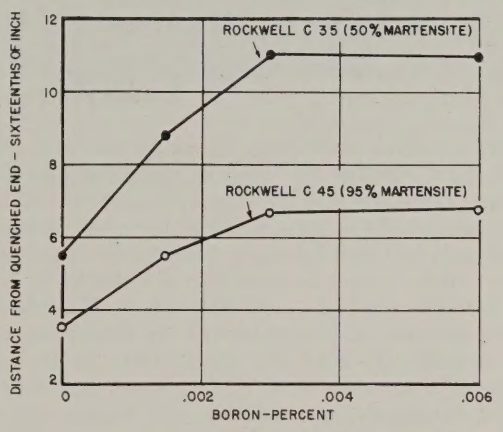
Variations from nil to 0.006 percent of boron additions made with either simple or complex intensifiers had no significant influence on the following properties of the steels: (1) Cleanliness, except titanium or zirconium inclusions in some steels treated with complex intensifiers (nonmetallic inclusions), (2) hot working (experimental steels), (3) transformation temperatures, (4) resistance to softening by tempering, (5) weldability (experimental steels), and (6) tensile properties of fully hardened and tempered specimens, except possibly an improvement in ductility when tempered at low temperatures.

Boron lowers the coarsening temperature of austenite. However, steels with relatively high additions of boron can be rendered fine grained at heat-treating temperatures by the judicious use of grain-growth inhibitors such as aluminum, titanium, and zirconium.

The influence of boron on hardenability and on notch toughness (Charpy impact, V-notched specimens) of fully hardened and tempered steels varied with the base composition of the steels, the composition of the intensifiers, and the amount of boron present. The increase in hardenability due to boron was greater for basic open-hearth than for experimental steels prepared in an induction furnace. The notch toughness at room and low temperatures of the commercial steels fully hardened and tempered at high temperatures was also superior to that of the experimental steels of similar composition heat-treated alike.

The hardenability, as determined by the end-quench test, of many of the experimental and all the steels comprising a basic open-hearth heat were markedly improved by additions of boron. However, no definite correlation was found between the hardenability effect and the amounts of boron added or retained in the steels. In many of the experimental steels the optimum hardenability was obtained with small additions of boron (0.001 percent or less retained), and in other steels the hardenability increased continuously with increase in boron. In other steels, the addition of boron as a simple or complex intensifier was either without effect or impaired the hardenability. In general, relatively





Although relative hardenability of boron-treated steels is indicated by comparison of Jominy curves (upper), it is more convenient to show the hardenability effect due to boron by comparing distances from the quenched end of the Jominy bars corresponding to selected hardness values (lower.) Illustrated are curves for steels containing 0.30 percent of carbon and 1.6 percent manganese, deoxidized with 0.10 percent of aluminum before adding boron—steel No. 1 contained no boron; No. 2, 0.0015 percent; No. 3, 0.0030 percent; and No. 4, 0.0060 percent boron. Specimens were normalized at 1,650° F. and end-quenched from 1,575° F. ASTM grain numbers at 1,575° F. for the four steels were respectively 8, 7, 7, and 6.

small additions were more effective than large, and the complex intensifiers were more effective than the simple ones. The effectiveness of boron in enhancing the hardenability increased with the amounts (within limits) of manganese, chromium, and molybdenum. The hardenability of the boron-treated steels also varied with the state of deoxidation of the heat, and the final nitrogen content. High soluble nitrogen (and possibly oxygen) was detrimental to the boron effect on hardenability, but it was possible to retain the effect in high-nitrogen steels (low soluble nitrogen) by fixing the nitrogen with strong nitride-forming elements such as titanium or zirconium.

For the commercial steels, the magnitude of the hardenability effect was independent of the amount of boron added or retained and the composition of the intensifiers.

The hardenability of some of the experimental and commercial steels treated with boron was affected by variation in quenching temperatures. In certain steels, the degree of hardenability was increased by increasing

the quenching temperature above the usual recommended range, whereas in other steels the hardenability was not affected or was decreased by this change. The magnitude of the hardenability effect due to boron appears to depend upon the form in which it exists in austenite; not necessarily upon the total amount present.

The addition of small amounts of boron was often beneficial to the notch toughness at room temperature of the steels when fully hardened and tempered at low temperatures. When the steels were fully hardened and tempered at high temperatures the presence of boron, especially as relatively high additions with intensifiers containing titanium, was usually either without effect or was detrimental to notch toughness at room and subzero temperatures. Appreciable amounts of boron were retained in steel after remelting in an induction furnace under both normal and highly oxidizing conditions.

Clay Crucibles for High-Density Glasses, Glazes, and Enamels

Clay crucibles possessing properties that make them particularly suitable for smelting high-lead glazes and enamels, materials that are especially corrosive to ordinary clay crucibles, have resulted from two recent developments of the Bureau's refractories laboratory. One of these, a new composition for the body of the crucible, gives an improved structure. The other, an additional step in the procedure for lining crucibles, aids in sealing invisible, incipient cracks in the lining. The usual clay crucible is quite porous and therefore subject to penetration and attack by highly corrosive melts. By contrast, the pores in the new crucible are very small, and the interconnecting passages between them so minute that they effectively resist the flow of molten fluids.

The manufacture of high-quality glass calls for pots or crucibles that will resist attack from the molten glass and that will not introduce impurities through interaction with the glass. To meet the exacting requirements peculiar to the production of optical glass, the refractories laboratory has for over 20 years been engaged in research on refractory clay pots, techniques for their manufacture, and special compositions for particular applications. All of the pots used by the Bureau's optical glass plant, during capacity operation in both wars and pilot operations in other years, have been manufactured by the refractories laboratory. In fact, observations of the performance of pots in the plant have afforded an exceptional opportunity for the study

Clay crucibles for melting glasses, glazes, and enamels are prepared at the Bureau by the process of slip casting. For the more corrosive materials, crucibles are lined with a dense, low-porosity lining that is applied to the core of the mold (left) before the crucible is cast (center). Eight hours after casting, the core is removed (right). An additional step just developed consists in spraying a coat or coats of slip over the lining to aid in sealing invisible, incipient cracks.

Composition of refractory clay crucibles for highly corrosive glasses, glazes, and enamels

Material	Amount
	Percent
North Carolina kaolin	11
Georgia kaolin	9
Tennessee No. 5 ball clay	10
Kentucky No. 4 ball clay	10
Grog (reclaimed shell from used pots):	
Passing No. 10, retained on No. 20	13.1
Passing No. 20, retained on No. 40	9.7
Passing No. 40, retained on No. 100	13.8
Passing No. 100	23.4
Silicate of soda [a]	.025
Sodium carbonate [a]	.012

[a] Deflocculants, added as solutions. To 100 lb of dry batch are added 57 ml of a 10-percent solution of sodium carbonate, 115 ml of silicate of soda (Philadelphia Quartz Co. "S" brand or equivalent) and 2.56 gallons of water.

and correction of defects in pot structure, and have led to improvements in the quality of the glass.

For most glasses that have been produced, two types of pots have generally been satisfactory.[5] One of these, containing a dense low-porosity lining, has been used for manufacture of the more corrosive glasses, the other without a lining for those less corrosive. Several unique procedures developed at the Bureau are followed in the manufacture of these pots. The technique of slip-casting, first reported nearly 30 years ago, is used exclusively in preference to hand-molding methods. In this method the clay casting slip, that is, the mixture of dry ingredients with the proper amounts of deflocculants and water to give a good pouring consistency, is poured into plaster-of-paris molds. The molds consist of two parts, a shell and a core that is locked in position before the pot is cast. During the initial stage of casting, the mold is slightly tilted to lessen the tendency to entrap air bubbles between the lining and the pot. After the bottom is filled, the mold is brought level and rocked lightly until the pot is completely cast. Rocking serves the dual purpose of leveling the slip as it is cast and of freeing the air trapped in the slip during the casting operation.

Lining of the pots is in effect applied before the pots are cast. In other words, the lining slip is first poured around the core of the mold, which is removed and transferred to the shell. The pot is then cast in the same manner as for unlined pots. Double and triple layers of lining, up to a total thickness of ¼ inch or more, are sometimes applied.

Crucibles are finished by cutting surplus material from the rim (foreground); note the lining on the inner edge of the roughened portion. Stirring thimbles (center background) are cast of the same composition as the crucibles and coated with lining slip.

The additional step that has recently been introduced in the procedure for lining crucibles consists in spraying a coat or coats of clay slip over the lining to seal incipient cracks. Although not visible in the dry state, these cracks often open during use and permit a fluid glass or glaze to penetrate into the walls or in some instances leak entirely through the crucible.

The cores are removed as soon as practicable after casting in order to prevent cracking of the lining—timing of this operation is critical—and the shells are removed when the pots have set sufficiently to retain their shape. The pots are then air-dried and, finally, immediately before use, are heated to approximately the temperature of the melt they are to contain. A carefully regulated heating schedule must be followed in this step, with the rise in temperature controlled in accordance with the relative speed with which the pot can be heated without damage through certain ranges.

The new crucible composition, originally developed for highly corrosive glasses, possesses several desirable properties in addition to its unusual pore structure. It has low gas permeability, even though it shows a porosity of 22 percent after firing at 1,435° C. Crucibles of this composition have somewhat lower resistance to thermal shock, but considerably greater resistance to corrosion.

[5] Slip casting of clay pots for the manufacture of optical glass at the National Bureau of Standards, NBS Circular C452.

NBS Scientists

Dr. E. U. Condon, Director of the Bureau, has been appointed by the President to represent the Department of Commerce on the Interdepartmental Committee for Scientific Research and Development. The Committee, which was recommended by the Steelman report* to "further the most effective administration of Federal scientific research and development activities", was established on December 24, 1947. It consists of representatives of the Departments of Agriculture, Commerce, Interior; the Army, Navy, Air Force, and the National Military Establishment; the Federal Security Agency; the Atomic Energy Commission; the National Advisory Committee for Aeronautics; the Veterans' Administration; and the Smithsonian Institution.

Commenting on the formation of this committee, the President stated, "The Interdepartmental Commit-

*Science and public policy: **1**, A program for the Nation* (U. S. Government Printing Office, Washington 25, D. C., 1947, 20 cents).

tee will perform for the entire Federal establishment functions similar to those now performed by committees and boards which coordinate research programs within single departments or among limited groups of departments. These functions will include review of administrative policies and techniques to increase the efficiency of scientific operations and examination of current policies and practices relating to Federal support of research carried on outside the Government. The Committee will encourage cooperation among the scientists of the various Government agencies and develop means by which information on research can be most effectively disseminated."

Dr. Wallace Reed Brode, internationally known chemist, has been appointed Associate Director of the Bureau, succeeding Dr. Hugh L. Dryden, who has become Director of Aeronautical Research of the National Advisory Committee for Aeronautics. Dr. Brode will act as liaison between the Bureau and the Department of National Defense, and will also coordinate Bureau research done for other Federal Departments. Dr. Brode comes to the Bureau from Ohio State University, where he has been professor of chemistry. He was a member of the London Mission of the Office of Scientific Research and Development in 1944–45, and became head of the Paris Office of this Mission shortly after the fall of Paris. Following the close of European hostilities, he served for a time as head of the Science Department, Naval Ordnance Test Station, Inyokern, Calif.

NBS Publications

Periodicals [6]

Journal of Research of the National Bureau of Standards, volume **40,** number 2, February 1948. (RP1858 to RP1864, inclusive.)

Technical News Bulletin, volume **32,** number 2, February 1948. 10 cents.

CRPL–D42. Basic Radio Propagation Predictions for May 1948. Three months in advance. Issued February 1948. 10 cents.

Nonperiodical

Research Papers [6 7]

RP1850. Vulcanization of synthetic rubbers by the Peachey process. Norman Bekkedahl, Fred A. Quinn, Jr., and Elmer W. Zimmerman. 10 cents.

RP1851. Measurement of ozone over the Organ Mountains, New Mexico. Ralph Stair. 10 cents.

RP1852. Note on volume effect in coiling molecules. Robert Simha. 5 cents.

RP1853. Dissociation of SF_6, CF_4, and SiF_4 by electron impact. Vernon H. Dibeler and Fred L. Mohler. 10 cents.

RP1854. Physical properties of electrodeposited chromium. Abner Brenner, Polly Burkhead, and Charles W. Jennings. 15 cents.

RP1855. Surface tension of compositions in the systems PbO–B_2O_3 and PbO–SiO_2. L. Shartsis, S. Spinner, and A. W. Smock. 10 cents.

RP1856. Expansion effects shown by some Pyrex glasses. Arthur Q. Tool and James B. Saunders. 15 cents.

RP1857. Cavity pressure method for measuring the gain of hearing aids. Edith L. R. Corliss and G. S. Cook. 10 cents.

Circulars [6]

C461. Selected values of properties of hydrocarbons. $2.75.

C463. Safety for the household. 75 cents.

Letter Circulars [8]

LC885. List of published material relating to home building and maintenance. (Supersedes LC856).

LC886. Technical radio broadcast services, radio station WWV. (Supersedes LC875).

LC887. European footwear sizes.

LC888. Furs: General information.

LC889. Home heating problems—List of publications and articles. (Supersedes LC855).

LC872. (Supplement No. 1). Gas turbines, jet propulsion, and rocket power plants—bibliography of unclassified books and reports. (Continuation to date.)

Articles by Bureau Staff Members in Outside Publications [9]

The infrared emission spectra of CO_2 and H_2O molecules. Earle K. Plyler. Science (1515 Massachusetts Avenue, NW, Washington 5, D. C.) **107,** 48 (1948).

Industrial adhesives, Parts 1 and 2. Nicholas J. DeLollis. Product Engineering (330 West Forty-second Street, New York 18, N. Y.) **18,** No. 11, 117 (November 1947) and **18,** No. 12, 137 (December 1947).

Nomograph for paint film calculations. Horace A. Berman. Analytical Chemistry (1155 Sixteenth Street, NW, Washington 6, D. C.) **19,** 915 (1947).

Heat of combustion and formation of 1,3,5,7-cycloöctatetraene and its heat of isomerization to styrene. E. J. Prosen, W. H. Johnson, and F. D. Rossini. J. Am. Chem. Soc. (1155 Sixteenth Street, NW, Washington 6, D. C.) **69,** 2068 (1947).

Assembly and testing of 52-foot laboratory adsorption column. Separation of hydrocarbons by adsorption. B. J. Mair, A. L. Gaboriault, and F. D. Rossini. Ind. and Eng. Chem. (1155 Sixteenth Street, NW, Washington 6, D. C.) **39,** 1072 (1947).

A "yardstick" for size. Mansfield Lonie. Institute News (2 Park Avenue, New York 16, N. Y.) **14,** No. 12, 8 (December 1947).

Synchronization of oscillators. R. D. Huntoon. Proc. Inst. Radio Eng. (1 East Seventy-ninth Street, New York 21, N. Y.) **35,** 1415 (1947).

Surface tension of compositions in systems PbO-B_2O_3 and PbO-SiO_2. L. Shartsis, S. Spinner ,and A. W. Smock. J. Am. Ceramic Soc. (2525 N. High Street, Columbus 2, Ohio) **31,** 23 (January 1948).

The status of engineering research in electronics. Harry Diamond. J. Engineering Education (University of Pittsburgh, Pittsburgh 13, Pa.) **38,** No. 1, 57 (September 1947).

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[6] Send orders for publications under this heading only to the Superintendent of Documents, Government Printing Office, Washington 25, D. C. Annual subscription rates: Journal of Research, $4.50 (foreign $5.50); Technical News Bulletin, $1.00 (foreign $1.35); Basic Radio Propagation Predictions, $1.00 (foreign $1.25). Single copy prices of publications are indicated in the lists.

[7] Reprints from January Journal of Research.

[8] Available on request from the National Bureau of Standards, Washington 25, D. C. Letter Circulars are prepared to answer specific inquiries addressed to the Bureau, and are sent only on request to persons having a definite need for the information. The Bureau cannot undertake to supply lists or complete sets of Letter Circulars or send copies automatically as issued.

[9] These publications are not available from the Government. Requests should be sent direct to the publishers.

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